Synthesis and Structure of Binuclear Single-Bridged Bis[(phosphane)gold(I)]halogenonium Complexes

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Reactions of $(R_3P)AuX$ (X = Cl, Br, I) with $[(R_3P)Au]^+$ BF_4^-, obtained from $(R_3P)AuCl$ and $AgBF_4$ in tetrahydrofuran, lead to cationic binuclear gold(I) complexes of the general formula $\{[(R_3P)Au]_2X\}^+$ BF_4^-. A number of chloro- (R = Ph, *o*-Tol, Mes, Bzl, Et), bromo- (R = Ph, *o*-Tol, Mes) and iodo-bridged (R = Ph, Mes) complexes of this type have been isolated and identified on the basis of their analytical and spectroscopic data. The crystal structure of bis[(triphenylphosphane)gold(I)]bromonium tetrafluoroborate was determined by single-crystal X-ray diffraction. The cations contain two-coordinate bromine atoms with an Au–Br–Au angle of 96.83(3)°

Mononuclear (phosphane)gold(I) halides $(R_3P)AuX$ (X = Cl, Br, I) are among the most important coordination compounds of univalent gold. They are used extensively as convenient starting materials for many other classes of mono- and polynuclear gold(I) complexes. A large number of different primary, secondary and tertiary phosphanes have been employed as ligands in order to tailor the chemical and physical properties of the complexes. In all cases where the structure has been determined, the halide ligands are in a terminal position trans to the phosphane at linearly two-coordinate gold atoms[1]. Association occurs through Au···Au contacts[2].

In 1979 Uson et al. reported[3] that the halide anions Cl, Br and I can also act as single-atom bridges between two gold(I) centers in the di(aurio)halogenonium salts $\{[(Ph_3P)Au]_2X\}^+$ A^- ($A = ClO_4$, BF_4), which are obtained from $(Ph_3P)AuX$ with one equivalent of $[(Ph_3P)Au]^+$ ClO_4^- or $[(Ph_3P)Au]^+$ BF_4^- respectively. In the crystals of $\{[(Ph_3P)Au]_2Cl\}^+$ ClO_4^- there are two independent A-shaped cations with Au–Cl–Au angles of 80.7 and 82.7°[4]. These values are associated with short Au···Au distances, of 3.035 and 3.085 Å, and are indicative of intramolecular bonding interactions between the two Au atoms. The results can thus be taken as an early example of gold nucleation at a strongly electronegative metalloid atom. Higher degrees of auration at chlorine, bromine or iodine have not yet been observed.

As part of the general investigation of gold clustering at metalloid centers[5] we have also revisited the halide anions as nucleation centers for $[LAu]^+$ units.

Preparation, Properties and Spectroscopic Data of the Compounds

Previous investigations considering compounds with halogen single-atom bridges between gold(I) centers were carried out only with triphenylphosphane as the auxiliary ligand. In order to broaden the scope of this work and to determine the effects of the nature of the halogen atom and the phosphane ligands, a study of a series of AuCl, AuBr and AuI complexes of various tertiary phosphanes was initiated.

The precursor molecules of the type $(R_3P)AuX$ are readily available by means of standard literature methods. It is most convenient and economical to prepare first the chloro complexes [from commercial $HAuCl_4(aq)$ and the phosphane] and convert these into the bromo and iodo complexes through metathesis reaction with alkali halides in a two-phase solvent mixture. [It should be noted that no $(R_3P)AuF$ complex has ever been obtained, and all attempts undertaken during the present study were also unsuccessful.]

Apart from known Cl^-, Br^- or I^- complexes, the compounds $[(o\text{-}Tol)_3P]AuBr$, $[(Mes)_3P]AuBr$ and $[(Mes)_3P]AuI$ were prepared for the first time (see Experimental).

The halide-bridged dinuclear complexes were synthesized from the 1:1 compounds $(R_3P)AuX$ by addition of one mol-equivalent of the corresponding tetrafluoroborate $[(R_3P)Au]^+$ BF_4^- in tetrahydrofuran or THF/CH_2Cl_2 mixed solvents at low temperatures (ca. −10°C). Solutions of these tetrafluoroborates were obtained from equimolar quantities of the chloro complex and $AgBF_4$ in tetrahydrofuran or dichloromethane. After removing the AgCl precipitate by filtration, the filtrate was used directly without any further work-up.

$$2\,(R_3P)AuCl + AgBF_4 \rightarrow \{[(R_3P)Au]_2Cl\}^+\ BF_4^- + AgCl$$

$$(R_3P)AuCl + AgBF_4 \rightarrow [(R_3P)Au]^+\ BF_4^- + AgCl$$

$$(R_3P)AuX + [(R_3P)Au]^+\ BF_4^- \rightarrow \{[(R_3P)Au)]_2X\}^-\ BF_4^-\ (X = Br, I)$$

The products were crystallized from dichloromethane by addition of a low-polarity solvent like pentane or diethyl ether. Yields were generally high and in excess of 75%. The compounds are colorless solids with high melting and decomposition temperatures. They are soluble only in polar solvents, preferably in di- or trichloromethane.

Complementing previous results, the two dinuclear *chloro*-bridged complexes $\{[(Et_3P)Au]_2Cl\}^+$ BF_4^- and

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$\{[(Bzl_3P)Au]_2Cl\}^+ BF_4^-$ have been prepared; these are the first tri*alkyl*phosphane compounds of this type. *Bromo*-bridged species could be obtained only with tri*aryl*phosphane ligands: $\{[(Ar_3P)Au]_2\mathbf{Br}\}^+ BF_4^-$, where Ar = Ph, *o*-Tol and Mes. Tri*alkyl*phosphane complexes proved to be unstable under comparable conditions. The triphenylphosphane compound was isolated as single crystals and its crystal structure determined (below). *Iodo*-bridged analogues $\{[(Ar_3P)Au]_2\mathbf{I}\}^+ BF_4^-$ are available only with Ar = Ph and Mes.

It thus appears that for the series of the title compounds the stability generally decreases along the series Cl→Br→I, and that triarylphosphane complexes are more robust than trialkylphosphane analogues. Bulky aryl phosphanes give the most stable products, probably owing to efficient steric shielding of the sensitive cations.

The compounds have been characterized by their solution NMR data. The ^1H and ^{13}C resonances show generally no anomalies. Only in the case of the tri(mesityl)phosphane complexes do the consequences of hindered arene rotation have to be considered in order to account for the extra line splitting or broadening.

In the ^{31}P-NMR spectra major chemical shift differences are observed on going from mono- to bis-coordinated halogen ligands, which makes ^{31}P-NMR spectroscopy the most valuable tool for identification of the products. The nature of the cations is confirmed independently by the field desorption mass spectrometric data. Elemental analyses have been provided for representative cases (see Experimental).

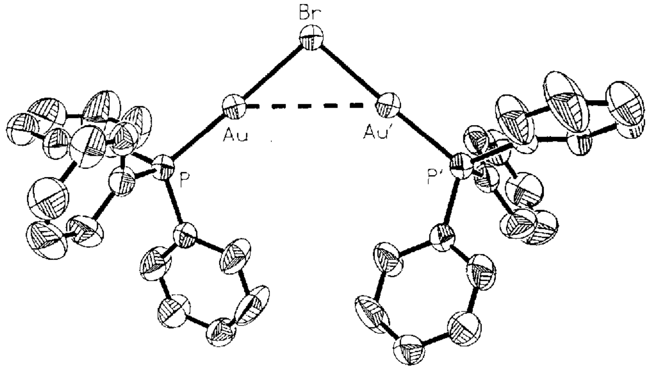
Crystal and Molecular Structure of $\{[(Ph_3P)Au]_2Br\}^+ BF_4^-$

Crystals of the compound obtained from CH_2Cl_2/Et_2O are monoclinic, space group *C*2/*c*, with *Z* = 4 formula units in the unit cell. The lattice contains no solvent molecules and is composed of independent anions BF_4^- and cations $\{[(Ph_3P)Au]_2Br\}^+$ with no sub van der Waals contacts. Both ions have crystallographically imposed C_2 symmetry.

For the cation the two-fold axis runs through the bromine atom bridging the two gold atoms. The Au–Br–Au′ angle is 96.83(3)°. The coordination at the gold atoms is quasi-linear, with angles P–Au–Br = 177.87(3)° and distances Au–P = 2.241(1) and Au–Br = 2.4384(6) Å. The quoted Au–Br–Au angle and the Au–Br distance are associated with an Au···Au′ distance of as much as 3.6477(1) Å, which is well beyond the limit of bonding interactions between the two metal atoms and is in the range of standard van der Waals contacts.

The structure of the bromo-bridged species is thus very different from that of the chloro analogue, which has an unusually compressed Au–Cl–Au angle of only 82.7(2)° and Au–Cl distances of 2.34(5) Å (average). This discrepancy can be accounted for by a simple geometrical reasoning: Attraction between two-coordinate gold(I) centers (auriophilicity) is known be strongest at distances in the range of 2.85–3.10 Å. At longer distances the energy contribution becomes negligible. For a 90° angle at Br (a reference to be adopted e.g. from H_2Se) and Au–Br distances of 2.438 Å (above), the Au···Au contact is calculated to be 3.447 Å, which is well beyond the auriophilicity limit. Even with a few degrees compression, the Au···Au distance cannot reach the "bonding" region. By contrast, for a 90° angle at chlorine (cf. H_2S) and Au–Cl bond lengths of 2.34 Å, the Au···Au distance is already 3.31 Å, and it needs only a 7° narrowing of the angle to reduce it to 3.06 Å (experimental value). For iodo-bridging, with even longer Au–I distances, no angles less than 90° are expected.

Figure 1. Structure of the cation in $\{[(Ph_3P)Au]_2Br\}^+ BF_4$ (ORTEP, 50% probability ellipsoids)[a]



[a] Selected bond lengths [Å] and bond angles [°]: Au–Br 2.4384(6), Au–P 2.2412(12), Au–Au 3.6477(1), Au–Br–Au′ 96.83(3), P–Au–Br 177.87(3).

Based on this reasoning it is tempting to ascribe the superior stability of the chloro-bridged compounds to the aurophilicity effect. Note that chlorine otherwise is expected to be a weaker donor and should give more labile complexes than bromine and iodine. The apparent nonexistence of the corresponding fluorine compounds is an intriguing phenomenon, however, which renders some of the arguments used above dubious and unsatisfactory. Clearly any entry to this white patch on the map of gold chemistry would be more than welcome.

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Experimental Section

All experiments were carried out under dry, purified nitrogen. Solvents were dried, distilled and stored over molecular sieves in a nitrogen atmosphere.

The complexes $(R_3P)AuCl$ (R = Ph[6], *o*-Tol[7], Mes[8], Bzl[9], Et[7]), $(Ph_3P)AuBr$[10] and $(Ph_3P)AuI$[10] were prepared according to established literature methods. The synthesis of $[(o\text{-}Tol_3)P]AuBr$, $[(Mes)_3P]AuBr$ and $[(Mes)_3P]AuI$ is described below.

NMR: Jeol GX 270, Jeol GX 400; $CDCl_3$ as solvent and internal standard, converted to TMS for ^1H and $^{13}C\{^1H\}$; H_3PO_4 (85%) as external standard for $^{31}P\{^1H\}$. – MS: Finnigan MAT 90 (field desorption).

[(o-Tol)$_3$P]AuBr: 805 mg (1.5 mmol) of $[(o\text{-}Tol)_3P]AuCl$ is dissolved in 20 ml of CH_2Cl_2 and 20 ml of an aqueous solution of 2.0 g (17 mmol) of KBr is added to the solution. The resulting two-phase system is stirred vigorously for 3 h. The aqueous layer is separated from the organic layer and washed with 10 ml of CH_2Cl_2.

The dichloromethane extracts are combined and dried with $MgSO_4$, and the solvent is evaporated under vacuum to leave a white crystalline product; yield 854 mg (98%), m.p. 262°C. – ^1H NMR: $\delta = 2.69$ (s, 3H, CH_3), 6.93–7.47 (m, 4H, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 23.3$ (d, $^3J_{C,P} = 11$ Hz, CH_3), 125.2 (d, $^1J_{C,P} = 60$ Hz, C^1), 126.7 (d, $^3J_{C,P} = 10$ Hz, C^5), 131.9 (d, $^4J_{C,P} = 3$ Hz, C^4), 132.4 (d, $^3J_{C,P} = 9$ Hz, C^3), 133.5 (d, $^2J_{C,P} = 9$ Hz, C^6), 142.9 (d, $^2J_{C,P} = 13$ Hz, C^2). – $^{31}P\{^1H\}$ NMR: $\delta = 12.1$ (s).

[(Mes)$_3$P]AuBr: 3.0 g (25 mmol) of finely pulverized KBr is suspended in a solution of 621 mg (1.0 mmol) of [(Mes)$_3$P]AuCl in 40 ml of THF. After stirring for 72 h at room temperature the solvent is removed under reduced pressure and the residue extracted with CH_2Cl_2 (3 × 20 ml). The combined CH_2Cl_2 extracts are concentrated under vacuum. Addition of pentane leads to precipitation of the white product, which is filtered off, washed with pentane and dried in a vacuum; yield 550 mg (83%), m.p. 270°C (dec.). – ^1H NMR: $\delta = 1.81$, 2.77 (br. s, 6H, $C^{2/6}{-}CH_3$), 2.27 (s, 3H, $C^4{-}CH_3$), 6.87 (br. s, 2H, $C^{3/5}{-}H$). – $^{13}C\{^1H\}$ NMR: $\delta = 20.9$ (s, $C^4{-}CH_3$), 23.9 (br. m, $C^{2/6}{-}CH_3$), 125.6 (d, $^1J_{C,P} = 53$ Hz, C^1), 131.7 (d, $^3J_{C,P} = 9$ Hz, $C^{3/5}$), 141.1 (br. m, $C^{2/4/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = -1.4$ (s).

[(Mes)$_3$P]AuI: Following the procedure given above using 3.0 g (18 mmol) of KI and 621 mg (1.0 mmol) of [(Mes)$_3$P]AuCl; yield 447 mg (63%), m.p. 259°C (dec.). – ^1H NMR: $\delta = 1.86$, 2.86 (br. s, 6H, $C^{2/6}{-}CH_3$), 2.28 (s, 3H, $C^4{-}CH_3$), 6.90 (br. s, 2H, $C^{3/5}{-}H$). – $^{13}C\{^1H\}$ NMR: $\delta = 20.9$ (s, $C^4{-}CH_3$), 23.6 (br. m, $C^{2/6}{-}CH_3$), 125.8 (d, $^1J_{C,P} = 52$ Hz, C^1), 131.7 (d, $^3J_{C,P} = 10$ Hz, $C^{3/5}$), 141.1 (br. m, $C^{2/4/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = 5.5$ (s). – $C_{27}H_{33}AuIP$ (712.40): calcd. C 45.52, H 4.67, Au 27.65, I 17.81; found C 44.72, H 4.46, Au 27.23, I 17.68.

General Procedure for {[(R$_3$P)Au]$_2$Cl}$^+$ BF$_4^-$: A solution of (R$_3$P)AuCl (0.4 mmol) in 10 ml of THF is added dropwise to a solution of $AgBF_4$ (39 mg, 0.2 mmol) in 10 ml of THF at 0°C to give a precipitate of AgCl. After stirring for 2 h at this temperature the mixture is filtered and the resulting clear solution evaporated to dryness under vacuum. The residue is recrystallized from dichloromethane/diethyl ether.

R = Ph: Yield 171 mg (82%), m.p. 177°C (dec.). – ^1H NMR: $\delta = 7.34$–7.58 (m, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 126.6$ (d, $^1J_{C,P} = 65$ Hz, C^1), 129.7 (d, $^3J_{C,P} = 13$ Hz, $C^{3/5}$), 132.9 (d, $^4J_{C,P} = 3$ Hz, C^4), 133.8 (d, $^2J_{C,P} = 14$ Hz, $C^{2/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = 31.4$ (s). – MS (FD), *m/z* (%): 955 (41) [M^+, ^{37}Cl], 953 (100) [M^+, ^{35}Cl].

R = o-Tol: Yield 180 mg (80%), m.p. 135°C (dec.). – ^1H NMR: $\delta = 2.53$ (s, 3H, CH_3), 6.97–7.62 (m, 4H, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 23.2$ (d, $^3J_{C,P} = 11$ Hz, CH_3), 123.2 (d, $^1J_{C,P} = 65$ Hz, C^1), 127.7 (d, $^3J_{C,P} = 11$ Hz, C^5), 133.1 (d, $^3J_{C,P} = 9$ Hz, C^3), 133.3 (d, $^4J_{C,P} = 3$ Hz, C^4), 134.0 (d, $^2J_{C,P} = 10$ Hz, C^6), 142.7 (d, $^2J_{C,P} = 12$ Hz, C^2). – $^{31}P\{^1H\}$ NMR: $\delta = 2.7$ (s). – MS (FD), *m/z* (%): 1039 (12) [M^+, ^{37}Cl], 1037 (27) [M^+, ^{35}Cl]. – $C_{42}H_{42}Au_2BClF_4P_2$ (1124.94): calcd. C 44.84, H 3.76, Cl 3.15; found C 44.09, H 4.15, Cl 3.47.

R = Mes: Yield 185 mg (72%), m.p. 147°C (dec.). – ^1H NMR: $\delta = 1.77$, 2.56 (br. s, 6H, $C^{2/6}{-}CH_3$), 2.30 (s, 3H, $C^4{-}CH_3$), 6.85 (br. s, 2H, $C^{3/5}{-}H$). – $^{13}C\{^1H\}$ NMR: $\delta = 20.8$ (s, $C^4{-}CH_3$), 23.4, 25.0 (br. s, $C^{2/6}{-}CH_3$), 123.5 (d, $^1J_{C,P} = 59$ Hz, C^1), 132.1 (br. m, $C^{3/5}$), 142.3 (d, $^4J_{C,P} = 3$ Hz, C^4), 142.5 (br. m, $C^{2/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = -10.7$ (s). – MS (FD), *m/z* (%): 1207 (43) [M^+, ^{37}Cl], 1205 (100) [M^+, ^{35}Cl].

{[(Et$_3$P)Au]$_2$Cl}$^+$ BF$_4^-$: A solution of 140 mg (0.4 mmol) of (Et$_3$P)AuCl in 10 ml of THF is added dropwise to a solution of 39 mg (0.2 mmol) of $AgBF_4$ in 10 ml of THF at −10°C. After stirring for 1 h at this temperature the precipitate of AgCl is filtered off and the colorless filtrate is concentrated under vacuum. On addition of diethyl ether a white precipitate is obtained, which is filtered off and dried in a vacuum; yield 93 mg (62%). – ^1H NMR: $\delta = 1.20$ (dt, $^3J_{H,P} = 20$, $^3J_{H,H} = 8$ Hz, 3H, CH_3), 1.99 (dq, $^2J_{H,P} = 11$, $^3J_{H,H} = 8$ Hz, 2H, CH_2). – $^{13}C\{^1H\}$ NMR: $\delta = 9.2$ (s, CH_3), 17.7 (d, $^1J_{C,P} = 37$ Hz, CH_2). – $^{31}P\{^1H\}$ NMR: $\delta = 34.6$ (s). – MS (FD), *m/z* (%): 667 (30) [M^+, ^{37}Cl], 665 (100) [M^+, ^{35}Cl].

{[(Bzl$_3$P)Au]$_2$Cl}$^+$ BF$_4^-$: A solution of 107 mg (0.2 mmol) of (Bzl$_3$P)AuCl in 15 ml of CH_2Cl_2 is added dropwise to a solution of 20 mg (0.1 mmol) of $AgBF_4$ in 5 ml of THF at 0°C to give a precipitate of AgCl, which is removed by filtration after stirring the mixture for 1 h at this temperature. The resulting clear solution is concentrated under vacuum. Addition of diethyl ether leads to precipitation of the white product, which is filtered off and dried under vacuum; yield 73 mg (65%), m.p. 181°C (dec.). – ^1H NMR: $\delta = 3.29$ (d, $^2J_{H,P} = 12$ Hz, 2H, CH_2), 7.27 (s, 5H, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 32.7$ (d, $^1J_{C,P} = 31$ Hz, CH_2), 128.1 (d, $^5J_{C,P} = 4$ Hz, C^4), 129.6 (d, $^4J_{C,P} = 3$ Hz, $C^{3/5}$), 130.5 (d, $^3J_{C,P} = 6$ Hz, $C^{2/6}$), 132.5 (d, $^2J_{C,P} = 5$ Hz, C^1). – $^{31}P\{^1H\}$ NMR: $\delta = 36.8$ (s). – MS (FD), *m/z* (%): 1039 (8) [M^+, ^{37}Cl], 1037 (20) [M^+, ^{35}Cl].

General Procedure for the Preparation of {[(R$_3$P)Au]$_2$Br}$^+$ BF$_4^-$: A solution of (R$_3$P)AuCl (0.2 mmol) in 10 ml of THF is added to a solution of $AgBF_4$ (39 mg, 0.2 mmol) in 5 ml of THF and the reaction mixture is stirred for 15 min at −10°C. The AgCl precipitate is removed and the clear, colorless filtrate added dropwise to a solution of (R$_3$P)AuBr (0.2 mmol) in 20 ml of THF. After stirring for 1 h at room temperature the solution is evaporated to dryness. The residue is dissolved in a minimum volume of CH_2Cl_2 and diethyl ether is added. A white precipitate of the product is formed, which is filtered off and dried in vacuo.

R = Ph: Yield 165 mg (76%), m.p. 167°C (dec.). – ^1H NMR: $\delta = 7.34$–7.59 (m, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 127.2$ (d, $^1J_{C,P} = 64$ Hz, C^1), 129.7 (d, $^3J_{C,P} = 12$ Hz, $C^{3/5}$), 132.8 (d, $^4J_{C,P} = 3$ Hz, C^4), 133.9 (d, $^2J_{C,P} = 14$ Hz, $C^{2/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = 33.8$ (s).

R = o-Tol: Yield 157 mg (67%), m.p. 128°C (dec.). – ^1H NMR: $\delta = 2.47$ (s, 3H, CH_3), 6.91–7.52 (m, 4H, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 23.0$ (d, $^3J_{C,P} = 12$ Hz, CH_3), 123.3 (d, $^1J_{C,P} = 63$ Hz, C^1), 127.4 (d, $^3J_{C,P} = 11$ Hz, C^5), 132.8 (d, $^3J_{C,P} = 9$ Hz, C^3), 132.9 (d, $^4J_{C,P} = 3$ Hz, C^4), 133.5 (d, $^2J_{C,P} = 10$ Hz, C^6), 142.3 (d, $^2J_{C,P} = 12$ Hz, C^2). – $^{31}P\{^1H\}$ NMR: $\delta = 6.3$ (s). – MS (FD), *m/z* (%): 1083 (36) [M^+, ^{81}Br], 1081 (26) [M^+, ^{79}Br].

R = Mes: Yield 163 mg (61%), m.p. 142°C (dec.). – ^1H NMR: $\delta = 1.76$, 2.55 (br. s, 6H, $C^{2/6}{-}CH_3$), 2.31 (s, 3H, $C^4{-}CH_3$), 6.85 (br. s, 2H, $C^{3/5}{-}H$). – $^{13}C\{^1H\}$ NMR: $\delta = 20.9$ (s, $C^4{-}CH_3$), 23.6, 25.1 (br. s, $C^{2/6}{-}CH_3$), 123.8 (d, $^1J_{C,P} = 57$ Hz, C^1), 131.8, 132.5 (br. m, $C^{3/5}$), 142.3 (d, $^4J_{C,P} = 3$ Hz, C^4), 142.7 (br. m, $C^{2/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = -7.0$ (s). – $C_{54}H_{66}Au_2BBrF_4P_2$ (1337.71): calcd. C 48.49, H 4.97, Br 5.97; found C 48.70, H 5.35, Br 5.27.

General Procedure for the Preparation of {[(R$_3$P)Au]$_2$I}$^+$ BF$_4^-$: The reaction is carried out as described above using (R$_3$P)AuCl (0.2 mmol), $AgBF_4$ (0.2 mmol) and (R$_3$P)AuI (0.2 mmol).

R = Ph: Yield 179 mg (79%), m.p. 160°C (dec.). – ^1H NMR: $\delta = 7.42$–7.68 (m, arene H). – $^{13}C\{^1H\}$ NMR: $\delta = 128.3$ (d, $^1J_{C,P} = 60$ Hz, C^1), 129.4 (d, $^3J_{C,P} = 12$ Hz, $C^{3/5}$), 132.2 (d, $^4J_{C,P} = 3$ Hz, C^4), 134.0 (d, $^2J_{C,P} = 14$ Hz, $C^{2/6}$). – $^{31}P\{^1H\}$ NMR: $\delta = 38.0$ (s).

R = *Mes:* Yield 180 mg (65%), m.p. 148 °C (dec.). – ^{1}H NMR: $\delta = 1.83$, 2.57 (br. s, 6H, $C^{2/6}-CH_3$), 2.31 (s, 3H, C^4-CH_3), 6.85 (br. s, 2H, $C^{3/5}-H$). – $^{31}P\{^1H\}$ NMR: $\delta = 0.1$ (s).

Crystal Structure Determination: A suitable single crystal of $\{[(Ph_3P)Au]_2Br\}^+\ BF_4^-$ was sealed into a glass capillary and used for measurement of precise cell constants and for intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. Diffraction intensities were corrected for Lp and absorption effects. The structure was solved by direct methods and refined by full matrix least-squares calculations against F^2 [SHELXL-93]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and their isotropic thermal parameters were tied to that of the adjacent carbon atom by a factor of 1.5. Selected interatomic distances and angles are given in the figure caption. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405936, the names of the authors, and the full journal citation.

Crystal Data of $\{[(Ph_3P)Au]_2Br\}^+\ BF_4^-$: Monoclinic, space group *C2/c*, $a = 18.476(1)$ Å, $b = 17.019(1)$ Å, $c = 12.514(1)$ Å, $\beta = 117.56(1)°$, $V = 3488.5(4)$ Å^3, crystal dimensions 0.25 × 0.30 × 0.55 mm, $Z = 4$, $d_{calcd.} = 2.068$ g/cm^{-3}, $F(000) = 2040$ e, Enraf Nonius CAD4 diffractometer, Mo-K_α radiation ($\lambda = 0.71069$ Å), $T = -68$ °C. Empirical absorption correction [$T_{min} = 0.5286$, $T_{max} = 0.9979$, μ(Mo-K_α) = 96.9 cm^{-1}]. 6352 reflections measured, 3221 unique reflections from which 3307 [2881 with $F_o \geqslant 4\sigma(F_o)$] were used. 209 refined parameters, $wR2 = 0.0739$, $R1\ [F_o \geqslant 4\sigma(F_o)] = 0.0296$ $\{wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$, $R1 = \Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|$, $w = q/2\sigma^2(F_o^2) + (ap)^2 + bp$, $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0440$, $b = 2.7082\}$, $_{final} = +1.40/-1.20$ e Å^{-3} (located at the heavier atoms).

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